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Electronic absorption spectra of 2,3-; 2,4- and 3,4-dimethoxybenzaldehydes

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The electronic absorption spectra of 2,3-; 2,4- and 3,4- dimethoxybenzaldehydes have been recorded in iso-octane solution. With the help of experimental data, calculations of integrated absorption intensities, oscillator strengths and excited state energies have been made for the observed band systems.

1. Introduction

Robertson & Matsen (1950) have recorded the electronic absorption spectra of some substituted benzenes in solution phase. The wavelength shifts observed in different substituents have been discussed in terms of resonance and inductive effects. Garg (1951, 1953) has made a detailed study of the absorption spectrum of benzaldehyde in vapour phase and observed three band systems in it. In the case of *o*-, *m*- and *p*- methoxybenzladehydes (Jaiswal 1965; Dwivedi 1965) also, three band systems have been observed. These are located at 2400 Å(I), at 2900 Å(II) and at 3750 Å(III) respectively. Systems (I) and (II) are ascribed due to π–π^* transitions whereas system (III) is attributed to n–π^* transition. Similar studies for other mono-substituted benzaldehydes have also been carried out by several workers (Morton *et al* 1940, Grammaticakis 1953, Dearden *et al* 1959 and Padhye *et al* 1963). With a view to extend some such type of studies in the case of di-substituted benzaldehydes, in the present investigations, we have recorded the electronic absorption spectra of 2,3-; 2,4- and 3,4- dimethoxybenzaldehydes in iso-octane solution. The integrated absorption intensities, oscillator strengths and excited state energies have been calculated for the observed band systems by making use of experimental data.

2. Experimental Details

The electronic absorption spectra of 2,3-; 2,4- and 3,4- dimethoxybenzaldehydes were recorded in iso-octane solution on an Unicam SP-700 ultraviolet-cum visible spectrophotometer in the range 1900–3300 Å. In each case, a quartz cell

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of 0.5 cm thickness was used as the absorption column. The spectra were recorded for solutions of different concentrations. However, the solutions of the concentration 0.0156, 0.01508 and 0.01476 gm./lit. in 2,3-; 2,4- and 3,4- dimethoxybenzaldehydes respectively gave the well defined absorption bands. The specific traces of the ultraviolet absorption spectra of the three isomeric dimethoxybenzaldehydes are reproduced in figures 1a, 2a, and 3a.

The samples used in the present investigations were obtained by the courtesy of Fluka-AG, West Germany. These were of analytical grade having 99.9% purity. Further purification was not desired.

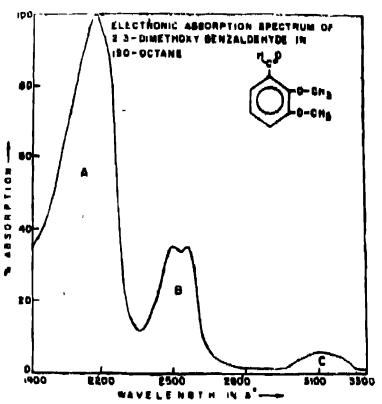

Fig. 1(a). U. V. absorption spectrum of 2,3-dimethoxy benzaldehyde.

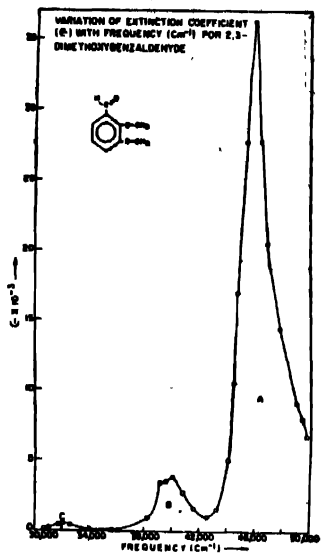

Fig. 1(b). Curve for the variation in extinction coefficient of 2,3-dimethoxy benzaldehyde.

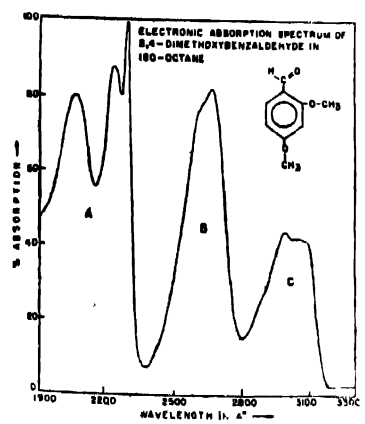

Fig. 2(a). U. V. absorption spectrum of 2,4-dimethoxy benzaldehyde.

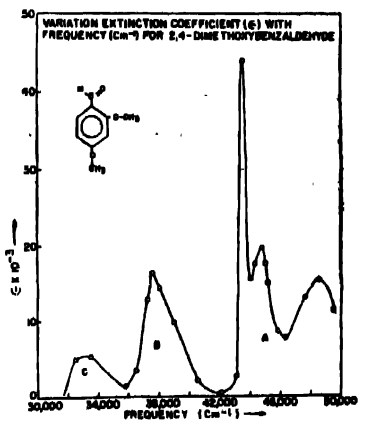

Fig. 2(b). Curve for the variation in extinction coefficient of 2,4-dimethoxy benzaldehyde.

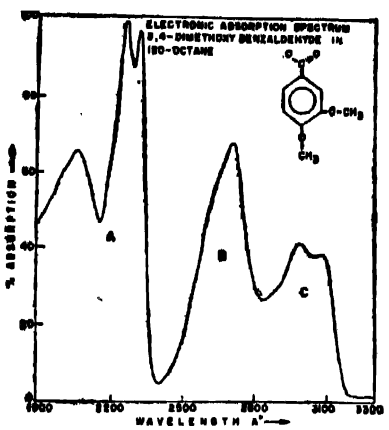

Fig. 3(a). U. V. absorption spectrum of 3,4-dimethoxy benzaldehyde.

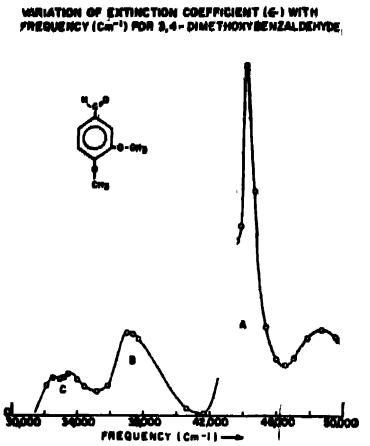

Fig. 3(b). Curve for the variation in extinction coefficient of 3,4-dimethoxy benzaldehyde.

3. Method of Calculation of Integrated-Absorption Intensities Oscillator Strength

The molar extinction coefficient ϵ, commonly used to measure the absorbion intensity is defined by

$$\frac{I}{I_0} = 10^{-\epsilon \cdot cd}$$

or

$$\epsilon = \left(\frac{1}{cd}\right) . \log \left(\frac{I_0}{I}\right), \qquad \ldots \quad (1)$$

where I_0 and I are the intensities of incident and transmitted beams respectively, c is the concentration of the solution in mole per litre and d is the thickness of the solution in cm (Higasi *et al* 1965).

The molar extinction coefficient is a function of frequency or wavelength. The oscillator strength associated with a particular electronic transition can be calculated with the help of integrated absorption intensity,

$$\int \epsilon(\bar{\nu}) d\nu, \qquad \ldots \quad (2)$$

where the integration is carried out over the whole frequency region associated with the particular absorption band. Thus, the oscillator strength for a particular transition is given by,

$$f = (10^3 \log 10)\frac{mc^2}{\pi e^2 n} \int \epsilon(\bar{\nu}) d\nu$$

$$= 4.32 \times 10^{-9} \int \epsilon(\bar{\nu}) d\nu. \qquad (3)$$

In this expression m is the electronic mass, e the electronic charge, ϵ the molar-extinction coefficient in litre mole^{-1}, N is the Avogadro's number and $\bar{\nu}$ is the frequency in wave number (cm^{-1}).

The integrated absorption intensity for a particular absorption band can be calculated with the help of a graph plotted between ϵ and ν.

4. Results and Discussions

In all these spectra, three absorption maxima are observed similar to the case of benzaldehyde (Garg 1951, 1953) and mono-subsitituted benzaldehydes (Jaiswal 1965, Dwivedi 1965, Padhey *et al* 1963). The three maxima have been found to lie in the regions (A) 2150–2300 Å, (B) 2550–2700 Å, and (C) 2950–3150 Å in all the three dimethoxybenzaldehyde isomers. As suggested by Jaiswal (1965) and Dwivedi (1965) for isomeric mono-methoxybenzaldehydes, in the present case also, it may be concluded that the first two band systems (A) and (B) correspond to π–π^* transition while the third band system (C) is due to n–π^* transition.

The variations of the extinction coefficient with respect to frequency (cm^{-1}) are shown in figures 1b, 2b, and 3b respectively for each of the three isomers of dimethoxybenzaldehyde. By measuring the areas of these curves with the help of a plani-meter, the integrated absorption intensities have been calculated

Table 1 Results of the electronic absorption spectra of 2,3-; 2,4- and 3,4- dimethoxybenzaldehydes in iso-octane solution.

Band system	Molecular constant	2,3-dimethoxy-benzaldehyde	2,4-dimethoxy-benzaldehyde	3,4-dimethoxy-benzaldehyde
A	Maximum	2175Å	2297Å	2256Å
	Integrated absorption intensity	106100	101800	104400
	Oscillator strength	0.00046	0.00044	0.00045
	Excited-state energy	5.6 ev	5.3 ev	5.4 ev
B	Maximum	2556 Å	2661 Å	2700 Å
	Integrated absorption intensity	12100	41800	30600
	Oscillator strength	0.000052	0.00018	0.00013
	Excited-state energy	4.8 ev	4.6 ev	4.5 ev
C	Maximum	3120 Å	2983 Å	2990 Å
	Integrated absorption intensity	1200	15000	14200
	Oscillator strength	0.0000052	0.000065	0.000061
	Excited-state energy	3.9 ev	4.1 ev	4.1 ev

for all the three band systems in each case. It is observed that the integrated absorption intensities vary in the order (A) > (B) > (C). Consequently, the change in oscillator strengths and excited-state energies are observed for each of the three isomers. The results are summarized in table 1.

It has been found in the case of electronic absorption spectra of substituted benzenes having mostly the *ortho-para directing* or the *electron-donor* groups that the band systems are displaced towards longer wavelength side. These shifts are generally accompanied with a change in the absorption intensities. The weaker intensity of the C-band system (n–π^* transition) in the case of 2,3-dimethoxybenzaldehyde as compared to the intensity of this band in 2,4- and 3,4-dimethoxybenzaldehydes may be explained due to increase in mesomeric interaction. It is usually observed that as the mesomeric interaction increases, the C-band system becomes less intense or even disappear.

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